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Synergistic Flame Retardant Effects between Aluminum Hydroxide and Halogen-Free Flame Retardants in High Density Polyethylene Composites

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Abstract

The synergistic flame retardant effects between aluminum hydroxide (ATH) and halogen-free flame retardants in high density polyethylene (HDPE) composites used for geo-grid were characterized by carrying out limited oxygen index (LOI) test, UL94 vertical burn test, alcohol blow 1amp test and cone calorimeter. The fire residue structure of the composites was examined by means of digital camera. The results indicate that there are obvious synergistic flame retardant effects between ATH and the halogen-free flame retardants including expandable graphite (EG) and Red phosphorus (RP). In comparison with ATH/RP system, ATH/EG system has good synergistic effect. Moreover, the synergistic effects of ATH/EG system can act better while further add RP. The LOI of ATH/EG/RP system can rise up to 30.1% and pass alcohol blow lamp test. However, no synergistic flame retardant effect is found between ATH and magnesium hydroxide (MH). Meanwhile, antagonistic effect is existed between ATH and zinc borate (ZnB). The analysis of fire residues show that the formation of char residues of ATH synergistic flame retardant systems act as an effective barrier to reduce the heat release rate and mass loss rate of the composites in condensed phase.

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Keywords: High density polyethylene, halogen-free flame-retardant, aluminum hydroxide, synergistic effect

1.Introduction

High density polyethylene (HDPE) is used more extensively in geo-grid to replace metal, fiber and wood, owing to its excellent mechanical properties, good insulating and corrosion resistance. However, the poor fire resistance of HDPE restricts its application in the units of high fire hazard areas such as coal mines. Incorporation of flame retardants has proved to be an effective way to reduce the flammability and smoke density of HDPE composites [1]. In general, halogen flame retardants show better behaviour in terms of flame retarded efficiency and mechanical property of HDPE composites used for geo-grid. However, the halogen flame retardants could create toxic and corrosive smoke in fire, processing limitations of evacuation. On the other hand, incorporation of inorganic metal hydroxide, red phosphorus (RP), zinc borate (ZnB) and expandable graphite (EG) can reduce effectively the fire hazards [2]. Aluminum hydroxide (ATH) as the most commonly used mineral flame retardants also can effectively reduce smoke production, but, because of the high load requires, processing a significantly decrease of the mechanical performance [3]. The ATH synergistic with halogen flame retardant, red phosphorus, zinc borate and expandable graphite can obvious improve the flammability, and decrease the loading of

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ATH which is help to increase the mechanical performance of HDPE composites [4]. The synergistic flame retardant system can act a combination of condensed and vapor phase mechanism, depending on both the ATH and the synergistic agents [5]. This paper aimed to analyze the synergistic flame retardant between ATH and other flame retardants including magnesium hydroxide (MH), RP, ZnB and EG in the HDPE composites used for geo-grid, and understand the mechanism of synergistic flame retardant systems.

2 Experimental

2.1.Materials

High impact polyethylene pellets were purchased from. Tai-an modern plastic company, China. Red phosphorus (RP), zinc borate (ZnB), Expandable graphite (EG) and aluminum hydroxide (ATH) were acquired from the Tianjin Guangcheng Chemical Co, Ltd, China.

2.2 Sample preparation

Before the experiment, all materials were dried at 80℃ for 8h. Formulated HDPE and different flame retardants were mixed at 160℃ for 20min using lab two-roll mill. Then they were molded into the sample sheets with dimensions of $100\times100\times4$ mm^3 for cone calorimeter tests, employing a high temperature press at 160℃.

2.3 Measurements

The Limited oxygen index (LOI) was measured using an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ASTM 2863. A vertical burning test was determined to use a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) according to the UL94 test standard. An alcohol blow 1amp test was measured an alcohol blow burner instrument (Jiangning Analysis Instrument Company, China) according to MT113-1995 - “common test methods and criteria for fire resistance and antistatic property of polymer products for underground coal mine application” organized by China. In the alcohol blow 1amp test, the polymer was rated mainly according to the recorded flaming time.

The cone calorimeter test was conducted using a FTT standard device (FTT, UK) according to ISO 5660 at an incident heat flux of $50kW/m^2$. $50kW/m^2$ heat flux represented a medium-scale fire similar to those on their way to full development [6]. In order to avoid overflow and dripping of molten thermoplastics, the aluminum foil used to contain the specimen, the thickness of the aluminum foil was about 10 mm deep, which was larger than that of specimen. A large number of parameters may be derived from cone calorimeter.

Table 1 Influences of halogen-free flame retardants on combustion parameters of HDPE/ATH composites

Compositions	LOI	UL94 rating	Rating and phenomenon of alcohol blow 1amp test
HDPE	17.5	HB	no rating, dropping with low speed
40%ATH	21.6	HB	no rating, dropping with low speed
20%ATH/20%MH	22.2	HB	no rating, burning out and dropping with low speed
40%MH	22.7	HB	no rating, burning out and dropping with low speed
35%ATH/5%EG	25.6	V-2	no rating, charring and burning out
35%ATH/5%RP	24.4	V-2	no rating, melting and dropping with low speed
35%ATH/5%ZnB	21.1	HB	no rating, melting and almost no dropping
30%ATH/5%EG/5%RP	30.1	V-0	qualified rating, charring and self-extinguish
30%ATH/5%EG/5%ZnB	25.2	HB	no rating, melting and burning out

3 Results and discussions

3.1 Limiting oxygen index. UL 94 and alcohol blow 1amp test

The LOI, UL94 rating and alcohol blow 1amp rating of ATH combined with RP, EG and ZnB respectively in HDPE composites are listed in Table 1. As shown in Table 1, it can be found that there are obvious synergistic flame retardant effects between ATH and the halogen-free flame retardants including expandable graphite and Red phosphorus. In comparison with ATH/RP system, ATH/EG system has good synergistic effect. Moreover, the synergistic effects of ATH/EG system can act better with further addition of RP. The LOI value of ATH/EG/RP is 30.1 and the UL94 rating acquire V-0 rating. On the contrary, the antagonistic effects are found between ATH combined with ZnB, and no synergistic effects between ATH and MH. As seen from the results of alcohol blow lamp test, it can be found that the charring and self-extinguish of flame retarded HDPE or the molten flame retarded HDPE dripped easily could pass alcohol blow lamp test.

3.2 Cone calorimeter test

Heat release rate

The heat release rate (HRR), especially peak HRR, has been recognized to be the most important parameter to characterize the flammability of materials in fires [7]. The HRR curves of HDPE composites are shown in Figure 1. As shown in Figure1, pure HDPE has a sharp and single HRR peak, and the PHRR is 1345kW/ m^2 at approximate 225s. When incorporation of flame retardants, the sharp HRR peak is disappear, and the peak heat release rates of HIPS composites containing 40%ATH, 35%ATH/5%EG, 35%ATH/5%RP, 30%ATH/5%EG/5%RP and 30%ATH/5%EG/5%ZnB are 543.9 kW/ m^2, 280.9 kW/ m^2, 442.5 kW/ m^2, 280.3 kW/ m^2, 314.6 kW/ m^2 respectively. Compared with pure HDPE, the peak heat release rates of the HDPE composites are reduced by 59.56% with 40%ATH, 79.12% for 35%ATH/5%EG, 67.10% for 35%ATH/5%RP, 79.16% for 30%ATH/5%EG/5%RP and 76.61% for 30%ATH/5%EG/5%ZnB. From the HRR curves, it can be seen that synergistic flame retardant systems reduces the initial peak effectively, which is generally ascribed to the formation of a char layer and consequent inhibition of volatile evaporation and heat transfer during burning [8]. In addition, the peak HRR of HDPE containing ATH combined with EG is obvious lower than ATH combined with RP, and incorporation of RP could further decrease the HRR of the HDPE composites containing ATH and EG, which is generally ascribed to the formation of a dense char residue. It is apparent from the dense char residues of the HDPE composites as shown in the photographs (see Figure 5). It is noted that the lower the HRR is, the better the UL94 rating obtained in synergistic flame retarded HDPE.

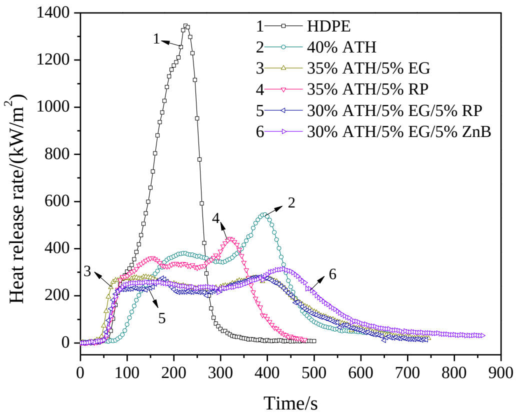

Fig.1 Heat release rate curves of flame retarded HDPE composites

Total heat release

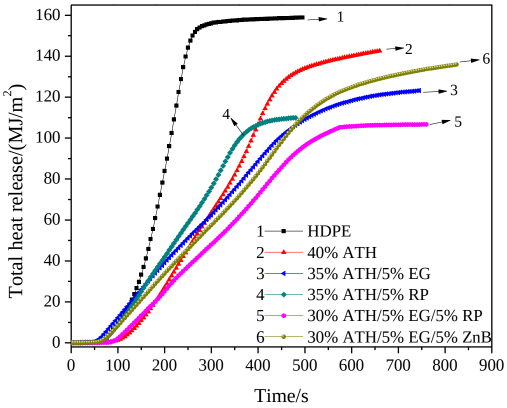

Fig.2 Total heat release curves of flame retarded HDPE composites

The total heat release (THR) of HDPE composites are shown in Figure 2. As shown in Figure 2, the distinction between pure HIPS and flame retarded HDPE composites is apparent after 150s. The THR value of pure HDPE is 158.9MJ/ m^2 which appears at approximate 250s. Incorporation of flame retardants, the THR values of composites are reduced significantly, and the THR of HDPE composites containing 40%ATH, 35%ATH/5%EG, 35%ATH/5%RP, 30%ATH/5%EG/5%RP and 30%ATH/5%EG/5%ZnB are 142.6 MJ/ m^2, 123.2 MJ/ m^2, 109.9 MJ/ m^2, 106.6 MJ/ m^2 and 139.3 MJ/m^2. Compared with pure HDPE, the THR values of the HDPE composites are reduced by 10.26% with 40%ATH, 22.47% for 35%ATH/5%EG, 30.84% for 35%ATH/5%RP, 32.91% for 30%ATH/5%EG/5%RP and 12.33% for 30%ATH/5%EG/5%ZnB. The lowest THR values of HDPE composites containing 30%ATH/5%EG/5%RP can ascribe to the combination of condensed and vapor phase mechanism, which EG can promote the formation of char residue and RP is active both in the gas and the condensed phase. On the contrary, ATH combined with zinc borate also has antagonistic effects in increasing the THR of HDPE composites.

Mass loss rate

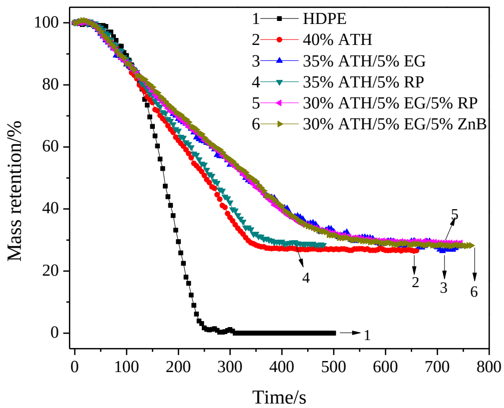

Fig.3 Mass retention curves of flame retarded HDPE composites

The mass retention curves of the HDPE composites are shown in Figure 3. As shown in Figure 3, the mass loss of pure HDPE is very high, and no residue remained after burning. On the contrary, it is obvious that the residual mass of flame retarded HDPE samples increase with the addition of ATH and synergistic agents. It should be figured out that the residual mass of flame retarded HDPE is close to the original loading levels of ATH and synergistic agents, indicating that the ATH and synergistic agents may not promote the charring of HDPE polymer matrix but generate a dense fire residue, which act as a protective barrier to reduce the heat and mass transfer [9].

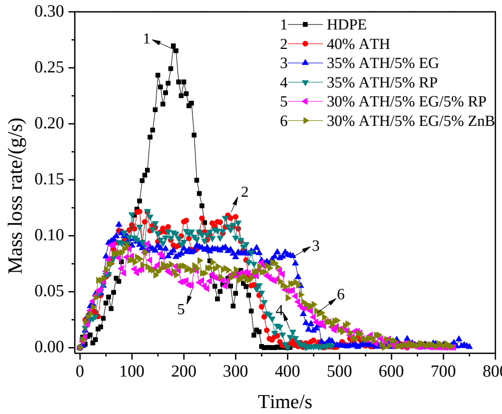

Fig.4 Mass loss rate curves of flame retarded HDPE composites

The mass loss rate curves of HDPE composites are shown in Figure 4. The HDPE incorporated with flame retardants ignited earlier than pure HDPE, resulting in an earlier mass reduction. However, the flame retardants reduce the mass loss rate (MLR) of composites after the initial decomposing stage at approximately 100s as shown in Figure 4. After the initial stage, the mass loss rates of HDPE composites are reduced significantly with addition of flame retardants. Compared with pure HDPE, a plateau or shoulder appears on the MLR curves, and the PMLR of the HDPE composites are obvious decreased with the addition of ATH and synergistic agents. From the MLR curve trend in Figure 4, it can be seen that with increasing char formation due to the ATH and synergistic agents which can be illustrated by the photos of char residues (see Figure 5), mass loss rate is reduced significantly during burning, which is similar to the results of HRR as shown in Figure 1.

3.3 Photographs of fire residue

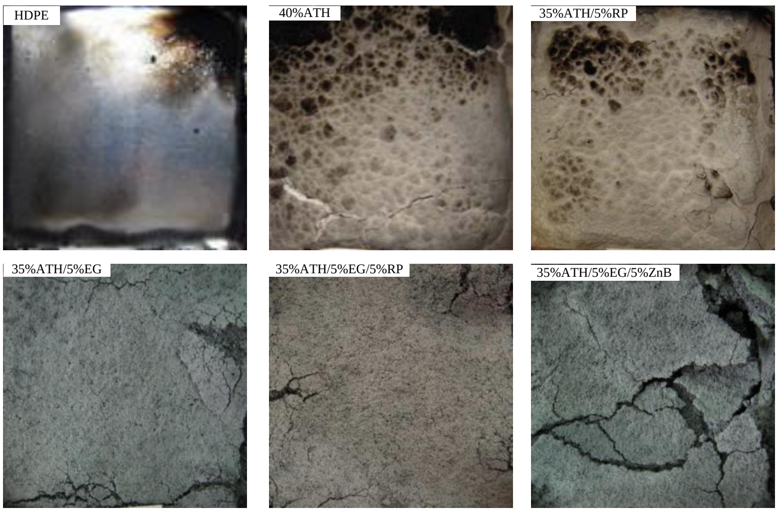

Fig.5 Photographs of fire residue of flame retarded HDPE composites

The main effects of ATH synergistic flame retardant system on the flammability of HDPE composites can be ascribed to the fire residues formed during combustion. For pure HDPE, no fire residue is left after burning as shown in Figure5. However, the samples containing ATH and synergistic agents left a considerable volume of char residue after burning, which nearly uniformly cover the surface of aluminum foil. It is noted that the surface of 40%ATH sample shows large cracks, which attributed to the higher HRR, THR and large mass loss, mass loss rate than ATH synergistic with RP or EG during burning. With addition of EG into ATH flame retarded HDPE, the fire residues become dense and thick as shown in Figure 5. The dense and thick can obviously improve the flammability of HDPE composites, which act as a good thermal insulation layer to hinder the heat transfer and permeability of gases [10, 11].

4 Conclusions

As to all the results of synergistic flame retarded HDPE composites by different fire tests, we can draw the following conclusions. The study shows that ATH can help to improving the flammability of HDPE composites in decreasing of heat release rate, total heat release and mass loss rate. With addition of inorganic flame retardants including RP and EG, the ATH flame retarded HDPE composites show obvious synergistic effects in improving the flame retardancy. However, there are no synergistic effects between ATH and MH, and ATH combined with zinc borate had antagonistic effects. Combination the fire residue of composites, it can be seen that the main flame retardant action of ATH synergistic systems occurs in the condensed phase. During burning, a large amount of fire residues are formed, which act as a physical barrier to hinder the heat transfer and volatile products. The dense and thick char residue has more effectiveness as a thermal shield to reduce the heat release rate and mass loss rate of the composites in condensed phase.

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